

SPECIFICATION

Electronic Version 1.2.8

Stylesheet Version 1.0

BARRIER LAYER FOR AN ARTICLE AND METHOD OF MAKING SAID BARRIER LAYER BY EXPANDING THERMAL PLASMA

Background of Invention

- [0001] The invention relates to a barrier layer that is resistant to the transmission of moisture and oxygen. More particularly, the present invention relates to an article having such a barrier layer and methods of applying such a barrier layer to an article.
- [0002] Different types of electronic devices such as, but not limited to, light emitting diodes (also referred hereinafter as "LEDs"), liquid crystal displays (also referred hereinafter as "LCDs"), photovoltaic articles, flat panel display devices, electrochromic articles, and organic electroluminescent devices (also referred hereinafter as "OELDs") share a common architecture: each device includes at least one substrate and at least one "active" layer.
- [0003] Many of the materials that are used in the active layers of such devices are sensitive to environmental factors. Electrode materials in LEDs and OELDs are sensitive to air and moisture, as are the polymeric and organic compounds that are used in OELDs and the liquid crystal materials in LCDs. Exposure to the elements – particularly oxygen and water – may severely limit the lifetime of such devices.
- [0004] Selection of a substantially impermeable substrate, such as glass, provides protection from environmental attack. Polymeric substrates that are used in flexible versions of such devices, however, do not provide adequate protection against oxygen

and moisture. Consequently, at least one coating that is substantially impermeable to oxygen and water vapor must be applied to the polymeric substrate to achieve the desired level of protection.

[0005] Barrier materials have been applied to substrates using a variety of coating processes. Plasma enhanced chemical vapor deposition (PECVD), for example, has been used to deposit barrier materials. Typical PECVD processes, however, are relatively slow; i.e. the barrier material is deposited on the substrate at a rate of about 30 to 60 nm/min or less. In order to be commercially viable, the barrier coating must be applied to the substrate at a significantly higher deposition rate.

[0006] While barrier materials are needed to extend lifetimes of flexible display devices such as LCDs, LEDs, and OLEDs to acceptable levels, the methods that are currently used to apply the needed barrier materials to substrates are too slow. Therefore, what is needed is a method of forming a barrier layer on a substrate at a high rate of deposition. What is also needed is a method of forming a barrier layer on a substrate to form an article having acceptable water vapor and oxygen transmission rates. What is further needed is an article having a barrier layer, the article having acceptable water vapor and oxygen transmission rates.

Summary of Invention

[0007] The present invention meets these and other needs by providing an article comprising a substrate having a barrier layer disposed on the surface of the substrate and methods of depositing such a barrier layer on the substrate, wherein the barrier layer is resistant to transmission of moisture and oxygen therethrough. The article may include additional layers, such as, but not limited to, an adhesion layer, abrasion resistant layers, radiation-absorbing layers, radiation-reflective layers, and conductive layers. Such articles include, but are not limited to, light emitting diodes (LEDs), liquid crystal displays (LCDs), photovoltaic articles, electrochromic articles, organic integrated circuits, and organic electroluminescent devices (OLEDs).

[0008] Accordingly, one aspect of the invention is to provide an article. The article comprises a substrate and at least one barrier layer disposed on at least one surface of the substrate, wherein the barrier layer comprises an inorganic material, and

wherein the barrier layer is resistant to transmission of moisture and oxygen therethrough and has a water vapor transmission rate (WVTR) at 25 ° C and 100% relative humidity of less than about 2 g/m^2 -day and an oxygen transmission rate (OTR) at 25 ° C and 100% oxygen concentration of less than about 2 cc/m^2 -day.

[0009] A second aspect of the invention is to provide a barrier layer that is resistant to transmission of moisture and oxygen therethrough. The barrier layer comprises at least one of a metal oxide, a metal nitride, a metal carbide, and combinations thereof. Each of the metal nitride, the metal carbide, and the metal oxide contains at least one of silicon, aluminum, zinc, indium, tin, a transition metal, and combinations thereof. The barrier layer has a water vapor transmission rate (WVTR) at 25 ° C and 100% relative humidity of less than about 2 g/m^2 -day and an oxygen transmission rate (OTR) at 25 ° C and 100% oxygen concentration of less than about 2 cc/m^2 -day.

[0010] A third aspect of the invention is to provide an article. The article comprises a substrate and at least one barrier layer, the at least one barrier layer comprising at least one of a metal oxide, a metal nitride, a metal carbide, and combinations thereof, wherein each of the metal nitride, the metal carbide, and the metal oxide contains at least one of silicon, aluminum, zinc, indium, tin, a transition metal, and combinations thereof, and wherein the barrier layer is resistant to transmission of moisture and oxygen therethrough and has a water vapor transmission rate (WVTR) at 25 ° C and 100% relative humidity of less than about 2 g/m^2 -day and an oxygen transmission rate (OTR) at 25 ° C and 100% oxygen concentration of less than about 2 cc/m^2 -day.

[0011] A fourth aspect of the invention is to provide a method of forming a coated article. The coated article comprises a substrate and a barrier layer disposed thereon, wherein the barrier layer is resistant to transmission of moisture and oxygen therethrough and has a water vapor transmission rate (WVTR) at 25 ° C and 100% relative humidity of less than about 2 g/m^2 -day and an oxygen transmission rate (OTR) at 25 ° C and 100% oxygen concentration of less than about 2 cc/m^2 -day. The method comprises the steps of: providing a substrate; generating a thermal plasma, the thermal plasma having an electron temperature of less than about 1 eV; injecting at least one reagent into the thermal plasma; reacting the at least one reagent in the thermal plasma to form at least one deposition precursor; and depositing the at least one deposition

precursor on the substrate at a rate of at least about 200 nm/min to form the barrier layer on the substrate.

[0012] A fifth aspect of the invention is to provide a method of forming a barrier layer on a substrate. The barrier layer is resistant to transmission of moisture and oxygen therethrough and has a water vapor transmission rate (WVTR) at 25 ° C and 100% relative humidity of less than about 2 g/m^2 -day and an oxygen transmission rate (OTR) at 25 ° C and 100% oxygen concentration of less than about 2 cc/m^2 -day, and comprises at least one of at least one of a metal oxide, a metal nitride, a metal carbide, and combinations thereof, wherein each of the metal nitride, the metal carbide, and the metal oxide contains at least one of silicon, aluminum, zinc, indium, tin, a transition metal, and combinations thereof. The method comprises the steps of: generating a thermal plasma, the thermal plasma having an electron temperature of less than about 1 eV; injecting a first reagent into the thermal plasma, the first reagent comprising at least one of silicon, aluminum, zinc, indium, tin, a transition metal, and combinations thereof; injecting a second reagent into the thermal plasma, the second reagent comprising at least one of oxygen, nitrogen, and ammonia; decomposing the first reagent and the second reagent in the thermal plasma to form a plurality of decomposition products; reacting the at least one reagent in the thermal plasma to form at least one deposition precursor; and depositing the at least one deposition precursor on the substrate at a rate of at least about 200 nm/min to form the barrier layer comprising at least one of a metal oxide, a metal nitride, a metal carbide, and combinations thereof on the substrate.

[0013] A sixth aspect of the invention is to provide a method of forming a coated article. The coated article comprises a substrate and a barrier layer disposed thereon. The barrier layer is resistant to transmission of moisture and oxygen therethrough and has a water vapor transmission rate (WVTR) at 25 ° C and 100% relative humidity of less than about 2 g/m^2 -day and an oxygen transmission rate (OTR) at 25 ° C and 100% oxygen concentration of less than about 2 cc/m^2 -day, and comprises at least one of a metal oxide, a metal nitride, a metal carbide, and combinations thereof, wherein each of the metal nitride, the metal carbide, and the metal oxide contains at least one of silicon, aluminum, zinc, indium, tin, a transition metal, and combinations thereof. The method comprises the steps of: providing a substrate; generating a thermal

plasma, the thermal plasma having an electron temperature of less than about 1 eV; injecting a first reagent into the thermal plasma, the first reagent comprising at least one of silicon, aluminum, zinc, indium, tin, a transition metal, and combinations thereof; injecting a second reagent into the thermal plasma, the second reagent comprising at least one of oxygen, nitrogen, and ammonia; reacting the first reagent and the second reagent in the thermal plasma to form at least one deposition precursor; and depositing the at least one deposition precursor on the substrate at a rate of at least about 200 nm/min, thereby forming the barrier layer comprising at least one of a metal oxide, a metal nitride, a metal carbide, and combinations thereof on the substrate.

[0014] These and other aspects, advantages, and salient features of the present invention will become apparent from the following detailed description, the accompanying drawings, and the appended claims.

Brief Description of Drawings

[0015] FIGURE 1 is a schematic representation of an article of the present invention;

[0016] FIGURE 2 is a schematic representation of a flexible liquid crystal display of the present invention;

[0017] FIGURE 3a is a schematic representation of a light emitting diode of the present invention;

[0018] FIGURE 3b is a schematic representation of a organic electroluminescent device of the present invention;

[0019] FIGURE 4 is a schematic representation of an expanding thermal plasma deposition system; and

[0020] FIGURE 5 is a plot of the water vapor transmission rate of a silicon nitride barrier layer of the present invention as a function of reagent flow rate.

Detailed Description

[0021] In the following description, like reference characters designate like or corresponding parts throughout the several views shown in the figures. It is also

understood that terms such as "top," "bottom," "outward," "inward," and the like are words of convenience and are not to be construed as limiting terms.

[0022] Several display devices such as, but not limited to, light emitting diodes (also referred hereinafter as "LEDs"), liquid crystal displays (also referred hereinafter as "LCDs"), photovoltaic articles, flat panel display devices, electrochromic articles, and organic electroluminescent devices (also referred hereinafter as "OELDs") share a common architecture: each device includes at least one substrate and at least one "active" layer. Light emitting diodes and organic electroluminescent devices, for example, may include a cathode layer, an electron transport layer, an emission layer, a hole transport layer, and an anode layer disposed on a substrate. Liquid crystal displays may include two substrates, each having an electrically conductive layer disposed thereon, and a liquid crystal layer sandwiched between the two substrates.

[0023] Many of the materials that are used in these devices may be adversely affected by environmental factors. Electrode materials in LEDs and OELDs are sensitive to air and moisture, as are the polymeric and organic compounds that are used in OELDs and the liquid crystal materials in LCDs. Exposure to the elements – particularly oxygen and water – may severely limit the lifetime of such devices.

[0024] Selection of a substantially impermeable substrate, such as glass, provides protection from environmental attack. Polymeric substrates that are used in flexible versions of such devices, however, do not provide adequate protection against oxygen and moisture. Consequently, at least one barrier layer that is substantially impermeable to oxygen and water vapor must be applied to the polymeric substrate to achieve the desired level of protection. Here, a coating, device, or coated substrate that is described as being "substantially impermeable" is understood as having a water vapor transmission rate (also referred hereinafter as "WVTR") and an oxygen transmission rate (also referred hereinafter as "OTR") of less than about $2 \text{ g/m}^2\text{-day}$ at 25°C and 100% relative humidity and less than about $2 \text{ cc/m}^2\text{-day}$ at 25°C and 100% oxygen concentration, respectively.

[0025] Referring to the drawings in general and to Figure 1 in particular, it will be understood that the illustrations are for the purpose of describing a preferred embodiment of the invention and are not intended to limit the invention thereto.

Figure 1 is a schematic representation of an article 100 of the present invention. Article 100 comprises a substrate 102 and at least one barrier layer 106 disposed on a surface of substrate 102. An additional layer 104, such as, but not limited to, an adhesion layer, may be optionally disposed between substrate 102 and the at least one barrier layer 106. Substrate 102 may comprise one of glass, a polymeric material, silicon, a metallic web, and fiberglass. Where substrate 102 is a polymeric material, substrate 102 comprises at least one of a polycarbonate, a polyethylene terephthalate, a polyethylene naphthalene, a polyimide, a polyethersulfone, a polyacrylate, a polynorbornene, and combinations thereof. In another embodiment, substrate 102 is a metallic web comprising one of aluminum and steel.

[0026] The at least one barrier layer 106 comprises an inorganic material and is resistant to the transmission of moisture and oxygen therethrough. The at least one barrier layer 106 has a WVTR of less than about 2 g/m^2 -day at 25°C and 100% relative humidity and an OTR of less than about 2 cc/m^2 -day at 25°C and 100% oxygen concentration. In a second embodiment, the at least one moisture layer 106 has a WVTR of less than about 1.7 g/m^2 -day at 25°C and 100% relative humidity and an OTR of less than about 0.21 cc/m^2 -day at 25°C and 100% oxygen concentration. In a third embodiment, the at least one barrier layer 106 has a WVTR of less than about 0.157 g/m^2 -day at 25°C and 100% relative humidity and an OTR of less than about 0.13 cc/m^2 -day at 25°C and 100% oxygen concentration. The at least one barrier layer 106 comprises at least one of a metal oxide, a metal nitride, a metal carbide, and combinations thereof, wherein the metal is one of silicon, aluminum, zinc, indium, tin, and a transition metal, such as, but not limited to, titanium. In one embodiment, the at least one barrier layer 106 comprises titanium oxide. In another embodiment, the at least one barrier layer 106 comprises silicon nitride. The at least one barrier layer 106 has a thickness in a range from about 10 nm to about 10,000 nm. In one embodiment, the at least one barrier layer has a thickness in a range from about 20 nm to about 500 nm.

[0027] Article 100 may further include at least one layer 110, which is disposed adjacent to the at least one barrier layer 106. Where article 100 is a LCD display, the at least one layer may include at least one transparent electrically conductive layer comprising an oxide of tin, cadmium, indium, zinc, magnesium, gallium, and combinations

thereof. Where article 100 is an LED or OLED, the at least one layer may include, for example, a cathode layer, an electron transport layer, an emission layer (in OLEDs), a hole transport layer, and an anode layer, wherein the electron transport and hole transport layers may be either organic or inorganic material, and wherein the emission layer comprises an organic material.

[0028] Figure 2 is a schematic representation of the structure of a flexible liquid crystal display of the present invention. Flexible LCD 200 comprises a center liquid crystal layer 212, a first and a second conductive layer 214, 216, a first and a second barrier layer 218, 220 and a first and a second polymeric substrate 222, 224. First polymeric substrate 222, first conductive layer 214 and first barrier layer 218 combine to form a first plate 225 and second polymeric substrate 224, second conductive layer 216 and second barrier layer 220 combine to form a second plate 227. First and second plates 225, 227 are disposed substantially parallel to one another and liquid crystal layer 212 is interposed therebetween. Flexible LCDs have been described in "A Transparent Flexible Barrier for Liquid Crystal Display Devices and Method of Making the Same," U.S. Patent Application 09/836,657, by Argemiro Soares DaSilva Sobrinho, which is incorporated herein by reference in its entirety.

[0029] Figures 3a and 3b are schematic representations of a light emitting diode (LED) and an organic electroluminescent device (OLED), respectively. In LED 300 (Figure 3a), barrier layer 312 is disposed on substrate 310. Anode 314 is disposed on barrier layer 312 opposite substrate 310. Hole transport layer 314, which comprises at least one of the n-type (negative charge accepting) semiconductors known in the art, such as, but not limited to, silicon doped with phosphorous, is disposed on top of – and in contact with – anode 314. Electron transport layer 316, comprising at least one the p-type (positive hole) semiconductors known in the art, such as, but not limited to, silicon doped with aluminum, is disposed on top of and in contact with hole transport layer 314. Cathode 318 is disposed on top of – and in contact with – electron transport layer 316.

[0030] OLED 350 (Figure 3b) also includes a substrate 360, barrier layer 362, anode 364, hole transport layer 366, electron transport layer 370, and cathode 372 in substantially the same relation as in LED 300, with the exception that emission layer

368 is disposed between hole transport layer 366 and electron transport layer 370. Hole transport layer 366, emission layer 368, and electron transport layer 370 each comprise an organic material in either molecular or polymeric form. Electron transport layer 370 and emission layer 368 may be combined into a single layer. Alternatively, hole transport layer 366, emission layer 368, and electron transport layer 370 may be combined into a single layer.

[0031] In other embodiments, the at least one layer 110 may comprise at least one of an adhesion layer, an abrasion-resistant layer, an ultraviolet radiation-absorbing layer, and an infrared radiation-reflecting layer. When the at least one layer 110 comprises an adhesion layer, which is intended to promote adhesion of barrier layer 106 to substrate 102, the adhesion layer comprises at least one of a metal in elemental form, a metal carbide, a metal oxycarbide, a metal oxide, a metal nitride, a metal oxynitride, and a metal carbonitride, wherein the metal is one of silicon, aluminum, titanium, zirconium, hafnium, tantalum, gallium, germanium, zinc, tin, cadmium, tungsten, molybdenum, chromium, vanadium, and platinum. Alternatively, the adhesion layer may comprise at least one of: amorphous carbon; a ceramic comprising at least one of glass, silica, alumina, zirconia, boron nitride, boron carbide, and boron carbonitride; a silicone; monomers; oligomers; a siloxane; a polymer; an epoxide; an acrylate; an acrylonitrile; a xylene; a styrene; and the like, as well as combinations thereof. When included in the at least one layer 110, the ultraviolet radiation-absorbing layer comprises at least one of titanium oxide, zinc oxide, cerium oxide, an ultraviolet radiation-absorbing organic material in either polymeric or molecular form, and combinations thereof. The infrared radiation-reflecting layer, when included in the at least one layer 110, comprises at least one of silver, aluminum, indium, tin, indium tin oxide, cadmium stannate, zinc, and combinations thereof.

[0032] In one embodiment, the at least one barrier layer 106 is interposed between the at least one layer 110 and substrate 102. In one embodiment, shown in Figure 1, the at least one layer 110 may be disposed between barrier layer 106 and a second barrier layer 105. In addition, the at least one layer 110 need only be disposed between a portion of barrier layer 106 and second barrier layer 105, as seen in Figure 1. Such a configuration provides all-around encapsulation and protection of the at least one layer 110 from exposure to water vapor and oxygen. In another embodiment, the at

least one layer 110 is interposed between the at least one barrier layer 106 and substrate 102 (as represented by 104 in Figure 1). One example of the latter embodiment is when the at least one layer 110 comprises an adhesion layer.

[0033] The present invention also includes a method of forming the article 100 having barrier layer 106 disposed on substrate 102, as described herein, and a method of forming barrier layer 106, which is described herein, on substrate 102. Barrier layer 106 is formed on substrate 102 by injecting at least one reactant gas into a plasma, which is generated by at least one plasma source. The at least one plasma source is preferably an expanding thermal plasma (also referred to hereinafter as "ETP") source that produces an expanding thermal plasma. Either a single plasma source or an array of a plurality of plasma sources may be used to generate the plasma. Systems having single and multiple plasma sources have been described in: "Protective Coating by High Rate Arc Plasma Deposition," U.S. Patent 6,110,544, by Barry Lee-Mean Yang et al.; "Apparatus and Method for Large Area Chemical Vapor Deposition Using Expanding Thermal Plasma Generators," U.S. Patent Application 09/681,820, by Barry Lee-Mean Yang et al.; "Large Area Plasma Coating Using Multiple Expanding Thermal Plasma Sources in Combination with a Common Injection Source," U.S. Patent Application 09/683,149, by Marc Schaepkens; and "Apparatus and Method for Depositing Large Area Coatings on Non-Planar Surfaces," U.S. Patent Application 09/683,148, by Marc Schaepkens, all of which are incorporated herein by reference in their entirety.

[0034] A schematic representation of an ETP deposition system having a single ETP source is shown in Figure 4. ETP deposition system 400 includes high pressure plasma chamber 410 and a low pressure deposition chamber 420, the latter containing substrate 424. ETP source 402 includes a cathode 404, an anode 406, and a plasma source gas inlet 408, of which the latter two are disposed in plasma chamber 410. The plasma source gas is an inert gas, such as a noble gas; i.e., argon, helium, neon, krypton, or xenon. Alternatively, chemically reactive gases, such as, but not limited to, nitrogen and hydrogen, may be used as the plasma source gas. Preferably, argon is used as the plasma source gas. A plasma 412, which is an expanding thermal plasma, is generated in ETP source 402 by striking an arc between cathode 404 and anode 406 while introducing the plasma source gas into the arc through plasma source gas

inlet 408.

[0035] Plasma chamber 410 and deposition chamber 420 are in fluid communication with each other through opening 418. Deposition chamber 420 is in fluid communication with a vacuum system (not shown), which is capable of maintaining the deposition chamber at a pressure that is lower than that of plasma chamber 410. In one embodiment, the deposition chamber 420 is maintained at a pressure of less than about 1 torr (about 133 Pa) and, preferably, at a pressure of less than about 100 millitorr (about 0. 133 Pa), while plasma chamber 410 is maintained at a pressure of at least about 0.1 atmosphere (about 1.01×10^4 Pa).

[0036] At least one reactant gas injector 422 is located in deposition chamber 420 for providing at least one reactant gas at a predetermined flow rate into the plasma generated by plasma source 402. The at least one reactant gas is provided through at least one reactant gas injector 422 to plasma 412 as the plasma 412 enters deposition chamber 420 through opening 418. The at least one reactant gas may comprise a single reactant gas or a mixture of reactant gases. The at least one reactant gas may be provided from a single reactant gas source or separate, multiple reactant gas sources to either a single reactant gas injector system or separate reactant gas injector systems.

[0037] In an ETP, a plasma is generated by ionizing the plasma source gas in the arc generated between the cathode and anode to produce a positive ion and an electron. The following reaction, for example, occurs when an argon plasma is generated:
[t1]



[0038] The plasma is then expanded into a high volume at low pressure, thereby cooling the electrons and positive ions. In the present invention, plasma 412 is generated in plasma chamber 410 and expanded into deposition chamber 420 through opening 418. As previously described, deposition chamber 420 is maintained at a significantly lower pressure than plasma chamber 410. Consequently, the electrons in the ETP are too cold and thus have insufficient energy to cause direct dissociation of the at least

one reactant gas within the ETP. Instead, the at least one reactant gas that is introduced into the plasma may undergo charge exchange and dissociative recombination reactions with the ions and electrons within the ETP to form at least one deposition precursor. In the expanded ETP, the positive ion and electron temperatures are approximately equal and in the range of about 0.1 eV (about 1000 K). In contrast to an ETP, other types of plasmas produce electrons having a sufficiently high temperature to substantially affect the chemistry of the plasma. In such plasmas, the positive ions typically have a temperature of greater than 0.1 eV, and the electrons have a temperature of at least 1 eV, or about 10,000 K.

[0039] Once injected into plasma 412, the at least one reactant gas undergoes a reaction within the ETP to form at least one deposition precursor. Such reactions may include, but are not limited to, charge exchange reactions, dissociative recombination reactions, and fragmentation reactions. The at least one deposition precursor that is formed within the ETP is then deposited on a surface of substrate 424 to form the barrier layer 106 on substrate 424.

[0040] The at least one deposition precursor is deposited on substrate 424 at a rate of at least about 200 nm/min to form the at least one barrier layer 106 on substrate 424, although higher deposition rates are within the scope of the invention. In one embodiment, for example, the at least one deposition precursor is deposited on substrate 424 at a rate of at least about 600 nm/min. In yet another embodiment, the at least one deposition precursor is deposited on substrate 424 at a rate of at least about 3,000 nm/min. In still yet another embodiment, the at least one deposition precursor is deposited on a surface of substrate 424 at a rate of at least about 10,000 nm/min.

[0041] As previously described, the at least one barrier layer 106 comprises at least one of a metal oxide, a metal nitride, a metal carbide, and combinations thereof, wherein the metal is one of silicon, aluminum, zinc, indium, tin, and a transition metal, such as, but not limited to, titanium. In these instances, the at least one reactant gas includes a first gaseous reagent comprising at least one of a silane, a metal vapor, a metal halide, and an organic compound of a metal, wherein the metal is one of titanium, zinc, aluminum, indium, and tin. Exemplary silanes include disilanes,

aminosilanes, and chlorosilanes. Exemplary organic compounds include titanium isopropoxide, diethyl zinc, dimethyl zinc, indium isopropoxide, indium tert-butoxide, aluminum isopropoxide, and combinations thereof. Exemplary metal halides include the chlorides of titanium, tin, and aluminum. The at least one reactant may also comprise elemental zinc, indium, tin, and aluminum in vapor form. The first gaseous reagent is injected into plasma 412 along with a second gaseous reagent comprising at least one of oxygen, nitrogen, hydrogen, water, and ammonia. In one particular embodiment, where the at least one barrier layer 106 comprises at least one of an oxide, a nitride, and a carbide of titanium, a first gaseous reagent comprising at least one of titanium chloride and titanium isopropoxide is injected into plasma 412 along with a second reagent, which, in addition to – or instead of – oxygen, nitrogen, hydrogen, water, and ammonia, may include propane, butane, acetylene, and the like, as well as combinations thereof. In another embodiment in which the at least one barrier layer 106 comprises at least one of an oxide, a nitride, and a carbide of silicon, a first gaseous reagent comprising at least one of a silane, a disilane, an aminosilane, and a chlorosilane is injected into plasma 412 along with the second reagent. For example, a silicon nitride barrier layer may be deposited by injecting silane (SiH_4), diluted in helium to a concentration of about 2% and ammonia into an expanding thermal argon plasma.

[0042]

As previously described, article 100 may further include at least one layer 110 in addition to the at least one barrier layer 106. In such instances, the method of forming the article 100 having barrier layer 106 disposed on substrate 102, and the method of forming barrier layer 106 on substrate 102, both of which are described herein, may further include at least one step in which the at least one layer 110 is applied to either substrate 102 or barrier layer 106. It will be appreciated by those skilled in the art that the method by which the at least one layer 110 is deposited will depend upon the nature and properties (e.g., composition, desired physical properties, and the like) of the at least one coating. The at least one layer 110 may be deposited using the ETP plasma apparatus and method described herein. Alternatively, the at least one layer 110 may be deposited using methods such as, for example, sputtering, evaporation, ion beam assisted deposition (IBAD), plasma enhanced chemical vapor deposition (PEVCD), high intensity plasma chemical vapor deposition

(HIPCVD) using either an inductively coupled plasma (ICP) or electron cyclotron resonance (ECR), and the like.

[0043] The following example serves to illustrate the salient features and advantages of the present invention.

[0044] Example 1

[0045] A polycarbonate substrate having a thickness of 30 mil (about 0.76 mm) was placed in the deposition chamber of a plasma deposition system similar to that described in the present application and schematically shown in Figure 4. The substrate was positioned at a working distance (WD) ranging from about 25 cm to about 60 cm from the expanding thermal plasma (ETP) source. The vacuum vessel was evacuated to a pressure of less than about 100 mTorr (millitorr), argon gas was flowed through into the plasma chamber and the ETP source at a rate in a range from about 2 slm (standard liters per minute) to about 3 slm, and the plasma source was ignited. The ETP operated at a current level in the range from about 40 A to about 70 A. The pressure within the plasma chamber was in the range from about 300 torr to about 800 torr, whereas the pressure within the deposition chamber was in the range from about 45 mtorr to about 100 mtorr. The pressure differential caused the argon thermal plasma to expand into the deposition chamber, where reagents, comprising silane diluted in helium to a concentration of about 2% and ammonia, were injected through a ring injector into the expanding argon thermal plasma. The reagents reacted with the ETP to form deposition precursors, which then combined to deposit a silicon nitride material barrier layer on the polycarbonate substrate at a deposition rate of at least 200 nm/min.

[0046] A plot of the water vapor transmission rate (WVTR) at 25 ° C and 100% relative humidity and 100% relative humidity of the silicon nitride barrier layer as a function of reagent (in this case, ammonia) flow rate is shown in Figure 5. The WVTR for an uncoated polycarbonate film having a thickness of 30 mil is also shown in Figure 5. As seen in Figure 5, a single 350 nm thick silicon nitride barrier layer deposited on a polycarbonate film having a thickness of about 30 mil reduces the WVTR to less than $0.2 \text{ g/m}^2\text{-day}$. The films are highly transparent and colorless; the polycarbonate film with the silicon nitride barrier layer has a transparency of at least 89% and a yellow-

index of less than 0.7.

[0047] While typical embodiments have been set forth for the purpose of illustration, the foregoing description should not be deemed to be a limitation on the scope of the invention. For example, articles, other than flexible LCD displays, LEDs and OLEDs, that comprise a substrate and a barrier having the properties described herein are also considered to be within the scope of the present invention. Such articles include, but are not limited to, photovoltaic devices, electrochromic devices, x-ray imaging devices, organic integrated circuits, and rigid-substrate display devices. Accordingly, various modifications, adaptations, and alternatives may occur to one skilled in the art without departing from the spirit and scope of the present invention.

11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
570
571
572
573
574
575
576
577
578
579
580
581
582
583
584
585
586
587
588
589
590
591
592
593
594
595
596
597
598
599
600
601
602
603
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779
780
781
782
783
784
785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
900
901
902
903
904
905
906
907
908
909
910
911
912
913
914
915
916
917
918
919
920
921
922
923
924
925
926
927
928
929
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947
948
949
950
951
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967
968
969
970
971
972
973
974
975
976
977
978
979
980
981
982
983
984
985
986
987
988
989
990
991
992
993
994
995
996
997
998
999
1000
1001
1002
1003
1004
1005
1006
1007
1008
1009
1010
1011
1012
1013
1014
1015
1016
1017
1018
1019
1020
1021
1022
1023
1024
1025
1026
1027
1028
1029
1030
1031
1032
1033
1034
1035
1036
1037
1038
1039
1040
1041
1042
1043
1044
1045
1046
1047
1048
1049
1050
1051
1052
1053
1054
1055
1056
1057
1058
1059
1060
1061
1062
1063
1064
1065
1066
1067
1068
1069
1070
1071
1072
1073
1074
1075
1076
1077
1078
1079
1080
1081
1082
1083
1084
1085
1086
1087
1088
1089
1090
1091
1092
1093
1094
1095
1096
1097
1098
1099
1100
1101
1102
1103
1104
1105
1106
1107
1108
1109
1110
1111
1112
1113
1114
1115
1116
1117
1118
1119
1120
1121
1122
1123
1124
1125
1126
1127
1128
1129
1130
1131
1132
1133
1134
1135
1136
1137
1138
1139
1140
1141
1142
1143
1144
1145
1146
1147
1148
1149
1150
1151
1152
1153
1154
1155
1156
1157
1158
1159
1160
1161
1162
1163
1164
1165
1166
1167
1168
1169
1170
1171
1172
1173
1174
1175
1176
1177
1178
1179
1180
1181
1182
1183
1184
1185
1186
1187
1188
1189
1190
1191
1192
1193
1194
1195
1196
1197
1198
1199
1200
1201
1202
1203
1204
1205
1206
1207
1208
1209
1210
1211
1212
1213
1214
1215
1216
1217
1218
1219
1220
1221
1222
1223
1224
1225
1226
1227
1228
1229
1230
1231
1232
1233
1234
1235
1236
1237
1238
1239
1240
1241
1242
1243
1244
1245
1246
1247
1248
1249
1250
1251
1252
1253
1254
1255
1256
1257
1258
1259
1260
1261
1262
1263
1264
1265
1266
1267
1268
1269
1270
1271
1272
1273
1274
1275
1276
1277
1278
1279
1280
1281
1282
1283
1284
1285
1286
1287
1288
1289
1290
1291
1292
1293
1294
1295
1296
1297
1298
1299
1300
1301
1302
1303
1304
1305
1306
1307
1308
1309
1310
1311
1312
1313
1314
1315
1316
1317
1318
1319
1320
1321
1322
1323
1324
1325
1326
1327
1328
1329
1330
1331
1332
1333
1334
1335
1336
1337
1338
1339
1340
1341
1342
1343
1344
1345
1346
1347
1348
1349
1350
1351
1352
1353
1354
1355
1356
1357
1358
1359
1360
1361
1362
1363
1364
1365
1366
1367
1368
1369
1370
1371
1372
1373
1374
1375
1376
1377
1378
1379
1380
1381
1382
1383
1384
1385
1386
1387
1388
1389
1390
1391
1392
1393
1394
1395
1396
1397
1398
1399
1400
1401
1402
1403
1404
1405
1406
1407
1408
1409
1410
1411
1412
1413
1414
1415
1416
1417
1418
1419
1420
1421
1422
1423
1424
1425
1426
1427
1428
1429
1430
1431
1432
1433
1434
1435
1436
1437
1438
1439
1440
1441
1442
1443
1444
1445
1446
1447
1448
1449
1450
1451
1452
1453
1454
1455
1456
1457
1458
1459
1460
1461
1462
1463
1464
1465
1466
1467
1468
1469
1470
1471
1472
1473
1474
1475
1476
1477
1478
1479
1480
1481
1482
1483
1484
1485
1486
1487
1488
1489
1490
1491
1492
1493
1494
1495
1496
1497
1498
1499
1500
1501
1502
1503
1504
1505
1506
1507
1508
1509
1510
1511
1512
1513
1514
1515
1516
1517
1518
1519
1520
1521
1522
1523
1524
1525
1526
1527
1528
1529
1530
1531
1532
1533
1534
1535
1536
1537
1538
1539
1540
1541
1542
1543
1544
1545
1546
1547
1548
1549
1550
1551
1552
1553
1554
1555
1556
1557
1558
1559
1560
1561
1562
1563
1564
1565
1566
1567
1568
1569
1570
1571
1572
1573
1574
1575
1576
1577
1578
1579
1580
1581
1582
1583
1584
1585
1586
1587
1588
1589
1590
1591
1592
1593
1594
1595
1596
1597
1598
1599
1600
1601
1602
1603
1604
1605
1606
1607
1608
1609
1610
1611
1612
1613
1614
1615
1616
1617
1618
1619
1620
1621
1622
1623
1624
1625
1626
1627
1628
1629
1630
1631
1632
1633
1634
1635
1636
1637
1638
1639
1640
1641
1642
1643
1644
1645
1646
1647
1648
1649
1650
1651
1652
1653
1654
1655
1656
1657
1658
1659
1660
1661
1662
1663
1664
1665
1666
1667
1668
1669
1670
1671
1672
1673
1674
1675
1676
1677
1678
1679
1680
1681
1682
1683
1684
1685
1686
1687
1688
1689
1690
1691
1692
1693
1694
1695
1696
1697
1698
1699
1700
1701
1702
1703
1704
1705
1706
1707
1708
1709
1710
1711
1712
1713
1714
1715
1716
1717
1718
1719
1720
1721
1722
1723
1724
1725
1726
1727
1728
1729
1730
1731
1732
1733
1734
1735
1736
1737
1738
1739
1740
1741
1742
1743
1744
1745
1746
1747
1748
1749
1750
1751
1752
1753
1754
1755
1756
1757
1758
1759
1760
1761
1762
1763
1764
1765
1766
1767
1768
1769
1770
1771
1772
1773
1774
1775
1776
1777
1778
1779
1780
1781
1782
1783
1784
1785
1786
1787
1788
1789
1790
1791
1792
1793
1794
1795
1796
1797
1798
1799
1800
1801
1802
1803
1804
1805
1806
1807
1808
1809
1810
1811
1812
1813
1814
1815
1816
1817
1818
1819
1820
1821
1822
1823
1824
1825
1826
1827
1828
1829
1830
1831
1832
1833
1834
1835
1836
1837
1838
1839
1840
1841
1842
1843
1844
1845
1846
1847
1848
1849
1850
1851
1852
1853
1854
1855
1856
1857
1858
1859
1860
1861
1862
1863
1864
1865
1866
1867
1868
1869
1870
1871
1872
1873
1874
1875
1876
1877
1878
1879
1880
1881
1882
1883
1884
1885
1886
1887
1888
1889
1890
1891
1892
1893
1894
1895
1896
1897
1898
1899
1900
1901
1902
1903
1904
1905
1906
1907
1908
1909
1910
1911
1912
1913
1914
1915
1916
1917
1918
1919
1920
1921
1922
1923
1924
1925
1926
1927
1928
1929
1930
1931
1932
1933
1934
1935
1936
1937
1938
1939
1940
1941
1942
1943
1944
1945
1946
1947
1948
1949
1950
1951
1952
1953
1954
1955
1956
1957
1958
1959
1960
1961
1962
1963
1964
1965
1966
1967
1968
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978
1979
1980
1981
1982
1983
1984
1985
1986
1987
1988
1989
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014
2015
2016
2017
2018
2019
2020
2021
2022
2023
2024
2025
2026
2027
2028
2029
2030
2031
2032
2033
2034
2035
2036
2037
2038
2039
2040
2041
2042
2043
2044
2045
2046
2047
2048
2049
2050
2051
2052
2053
2054
2055
2056
2057
2058
2059
2060
2061
2062
2063
2064
2065
2066
2067
2068
2069
2070
2071
2072
2073
2074
2075
2076
2077
2078
2079
2080
2081
2082
2083
2084
2085
2086
2087
2088
2089
2090
2091
2092
2093
2094
2095
2096
2097
2098
2099
2100
2101
2102
2103
2104
2105
2106
2107
2108
2109
2110
2111
2112
2113
2114
2115
2116
2117
2118
2119
2120
2121
2122
2123
2124
2125
2126
2127
2128
2129
2130
2131
2132
2133
2134
2135
2136
2137
2138
2139
2140
2141
2142
2143
2144
2145
2146
2147
2148
2149
2150
2151
2152
2153
2154
2155
2156
2157
2158
2159
2160
2161
2162
2163
2164
2165
2166
2167
2168
2169
2170
2171
2172
2173
2174
2175
2176
2177
2178
2179
2180
2181
2182
2183
2184
2185
2186
2187
2188
2189
2190
2191
2192
2193
2194
2195
2196
2197
2198
2199
2200
2201
2202
2203
2204
2205
2206
2207
2208
2209
2210
2211
2212
2213
2214